

THERMAL AND MECHANICAL PROPERTIES OF THE PRECURSOR POLYBLENDS: POLYHYDROXYAMIDE AND POLY(AMIC ACID)

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Abstract: A polyhydroxyamide (PHA) was synthesized. Blends of the PHA with poly(amic acid) (PAA) were prepared in DMAc. The presence of PHA enhanced the thermal and mechanical properties of the polyblends. All of the polyblended films show large endothermic peaks that decreased monotonically with increasing heat treatment temperature. The cyclization onset temperature (T_1), initial decomposition temperature (T_2), and weight residue at 900°C of the polyblends were shown to be in the ranges of 144-146°C, 532-540°C, and 44-45%, respectively. Also, the thermal stabilities were consistently enhanced with increasing annealing temperature from 25 to 250°C. The ultimate strength and initial modulus of the polyblends increased from 84 to 136 MPa and from 2.93 to 5.34 GPa, respectively, with increasing PHA content. Similar to the trend of thermal stability, increasing the annealing temperature of the polyblends increased the tensile properties of the films. The observed tensile properties are discussed in terms of the morphology of the fractured films as studied by scanning electron microscopy (SEM). The degree of crystallinity of the polyblends was characterized as a function of heat treatment temperatures by wide angle X-ray diffractometry (WAXD). Holographic interferometry is applied to precursor films to determine their biaxial stresses. Membranes for vibrational analysis are prepared using a circular precursor polymer. The biaxial stresses of the PHA, PAA, and 50/50 PHA/PAA are fairly constant with increasing frequencies: 6.85-7.61 MPa, 27.01-27.70 MPa, and 11.13-12.08 MPa, respectively. Regardless of the vibration modes, the biaxial stresses remain constant.

INTRODUCTION

Polybenzoxazoles (PBOs) (Akinseye et al., 1997) and polyimides (PIs) (Sroog, 1991) belong to a class of rigid-rod aromatic heterocyclic polymers which exhibit a high degree of orientation, high resistance to solvents, high glass transition temperature, high modulus, high strength, high thermal and thermooxidative stability, and low density. Despite their highly desirable properties, PBOs and PIs are essentially non-melting and exhibit poor solubility.

We have studied poly(amic acid) (PAA) and polyhydroxyamide (PHA) as high temperature precursor polymers (Chang et al., 1998). Compared with cyclized polymers, PI and PBO, these precursor polymers have greater solubility and processability. The greater solubility of the polymer precursors makes them a more practical starting point for preparing fibers, films, and molecular composites. Also, intense research on precursor has been devoted toward the development of more processable and soluble flame retardant polymers.

The problem with producing molecular composites is the phase separation of the rigid-rod component within polyblends. In order to eliminate the phase separation problem, a polymer precursor is combined with a matrix component and then thermally processed to convert the precursor into a rigid-rod cyclized polymer dispersed in the matrix (Harris et al., 1990). The in-situ schemes have the advantage of better compatibility of the precursor polymers with the matrix components over that of fully cyclized PBO or PI (Ree et al., 1998)

The use of precursor/precursor blends also avoids the processing disadvantages such as high pressures, strong solvents, and equipment erosion that occur when processing the cyclized polymers. However, there have been few studies concerned with how precursor polymer processing variables such as solvent concentration, processing temperature, and heat-treatment affect the mechanical properties of precursor/precursor blends.

The present work focuses on the thermal and mechanical properties of blends of PAA with PHA and compares the results with that of the pure precursor polymers. Holographic interferometry has been used extensively in various applications: the direct measurement of mechanical stresses (Maden, 1992), pressure stresses (Kussmaul and Ettemeyer, 1987), vibrational excitation (Fallstrom et al., 1989), swelling (Goldberg et al., 1975), and thermal stresses (Gilbert and Vedder, 1981). Holographic interferometry has also been used as a tool for stress measurement in polymer membranes (Maden, 1992).

An introduction to the holographic interferometry technique for measurement of biaxial stresses in precursor membranes is presented in this paper. Holographic interferometry is applied to measure the biaxial stresses of the precursor polymers and their polyblends.

EXPERIMENTAL

Materials

The precursor polymer, PHA, was prepared by solution polymerization (Chang et al., 1998) of the 3,3'-dihydroxybenzidine and isophthaloyl dichloride in N,N-dimethylacetamide

(DMAc). PAA used for this work was supplied by DuPont as a 15 wt% solution in DMAc. Table 1 shows the general properties of the precursor polymers. The chemical structures of PHA and PAA are as follows:

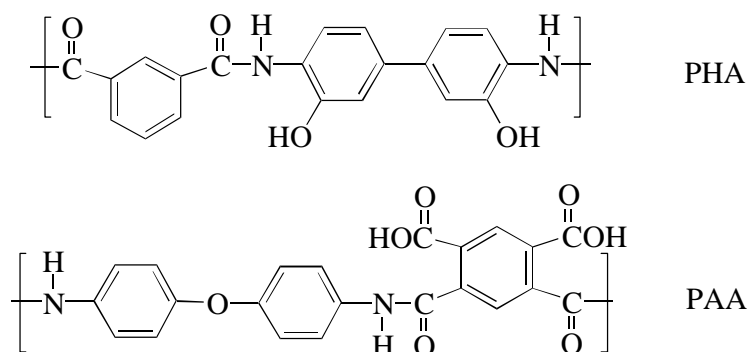


Table 1. General Properties of PHA and PAA

Polymer	IV ^a	T ^b , °C	ΔH ^c , J/g	T _d ^d , °C
PHA	1.32	319	221.1	577
PAA	2.01	178	122.1	533

^aInherent viscosity of the PHA was measured at 30 °C at 0.2 g/dL solution in NMP. Intrinsic viscosity of the PAA was measured at 30 °C by using 15 wt % solution in N,N-dimethyl acetamide (DMAc).

^bMinimum point in endothermic curve. ^cEndothermic enthalpy.

^dInitial decomposition temperature.

Film preparation

PHA and PAA in solution were mixed at room temperature. For each blend system, a solution in DMAc was prepared at various concentrations by mixing for one day under vigorous agitation. The concentration of the blended solution was 10% by weight. The polymer solution was coated onto a glass plate and dried in a vacuum oven at 60 °C for a day. Then the blended films, while still on the glass plates, were cleaned in an ultrasonic cleaner 5 times for 30 minutes each. These solvent-removed films were dried again in a vacuum oven at 60 °C for a day. The film thicknesses were typically in the range of 10-15 microns and were optically transparent for all compositions.

Characterization

The thermal behavior of the samples was studied by using a DuPont 910 differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). DSC and TGA

measurements were taken under a nitrogen atmosphere at a heating rate of 20 °C /min.

Wide angle X-ray diffractograms were obtained on a JEOL JDX-8D instrument using Ni-filtered Cu-K radiation. The scan speed was 4°/min.

All samples of the blended films were tested in tensile mode on an Instron mechanical tester, model No. 5564. The specimens were prepared by cutting 5 by 70 mm long strips. Tensile specimens were tested using a crosshead speed of 5 mm/min. A minimum of six samples was tested for each composition and average value and standard deviations were calculated from the data. Morphology of the fracture surfaces of blended films was prepared by fracture in liquid nitrogen followed by sputter-coating with gold. Fracture surfaces were viewed on a Hitachi-S 2400 scanning electron microscope (SEM).

Sample preparation for biaxial stress measurement

A rigid circular steel washer was adhered to the flat precursor film using Super Glue and pressure was applied to ensure uniform adherence. After the glue was dried, the films on the washer were soaked in an ultrasonic cleaner with absolute ethyl alcohol. The film was dried in a vacuum oven at 60 °C for a day in order to preserve the original state of stress.

Equipment for holographic interferometry

A membrane is placed in a fixture rigidly mounted in a Wilcoxon Research piezoelectric shaker, driven by a Wavetek Model 190 frequency generator connected to a Wilcoxon Research PA7 power amplifier. The frequency is monitored using a B & K Precision 80 MHz frequency counter. An image of the stationary membrane is recorded on a thermoplastic holographic plate using a Newport Research Corporation HC301 holographic camera. The light source used for this reflection hologram is a 5 mW helium-neon laser. A schematic of the holographic setup is shown in elsewhere (Chang et al., 1998).

RESULT AND DISCUSSION

Thermal properties

The thermal properties of the blended films were investigated for films annealed in a temperature range of 25-250 °C. The results are summarized in Table 2. Blends of PHA/PAA at room temperature showed two transitions in the DSC, one at 179 °C and the other at 316-318 °C for PHA contents in the range of 25-75%. These values are not different than the pure precursor polymers, which indicates that the two precursors are not miscible with each other at room temperature. (see Fig. 1).

Table 2. Thermal Properties of the Polyblend Films Annealed for 30 Minutes at Different Heat Treatment Temperatures

Annl. Temp °C	PHA/PAA wt%	T _c ^a °C	ΔH ^b J/g
25 (r.t.)	100/0	319	221.1
	75/25	179	12.4
	50/50	179	54.7
	25/75	179	107.0
	0/100	178	122.1
100	100/0	334	221.4
	75/25	262	215.8
	50/50	254	200.7
	25/75	238	93.5
	0/100	198	79.9
150	100/0	335	218.8
	75/25	308	210.8
	50/50	268	191.3
	25/75	259	80.4
	0/100	235	42.9
250	100/0	334	184.7
	75/25	302	144.9
	50/50	299	73.6
	25/75	303	36.3
	0/100	-	0

^aMinimum point in endothermic curve.

^bEndothermic enthalpy.

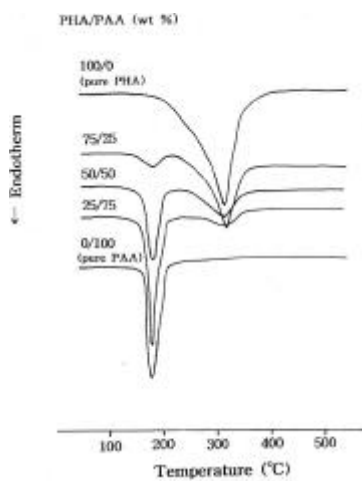


Figure 1. DSC thermograms of PHA, PAA and their polyblends.

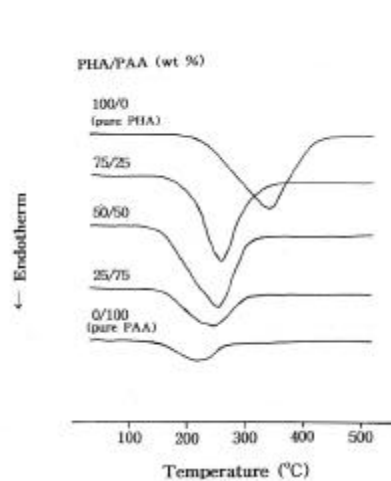


Figure 2. DSC thermograms of the polyblends annealed at 150 °C for 30 min.

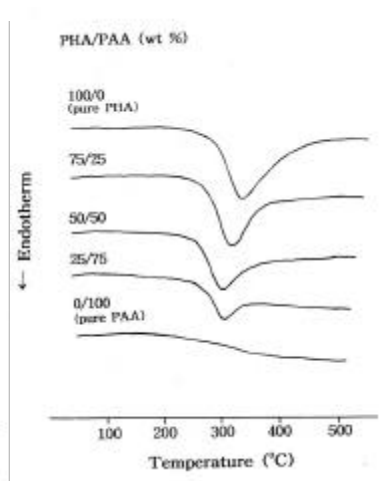


Figure 3. DSC thermograms of the polyblends annealed at 250 °C for 30 min.

For samples annealed in the range of 100-250 °C, there was only one peak in the DSC that shifted to higher temperatures with increasing annealing temperature. In particular, the higher

temperature transition of the 100/0 (pure PHA) occurred from 319 to 334 °C with increasing heat treatment up to 100 °C and then was constant above 100 °C. However for the case of 0/100 (pure PAA) composition, the endothermic minimum point increased from 178 to 235 °C with increasing annealing temperature from 25 to 150 °C, and then the endothermic peak disappeared for samples annealed above 250 °C as seen in Fig. 3. This suggests that PHA was not affected significantly depending upon annealing, whereas PAA becomes fully cyclized to the polyimide at 250 °C. The corresponding DSC profiles are shown in Fig. 1, 2, and 3 for comparison.

The endothermic enthalpies (ΔH) of the two precursors are much larger than those for other thermosetting polymers. Unlike other polymers, large heat capacities were shown at 221.1 J/g and 122.1 J/g for the PHA and PAA, respectively. Upon annealing, the endotherms (ΔH) for the pure precursors and blended composites are smaller than those of the unannealed samples, as listed in Table 2. This can be attributed to the cyclization reaction that usually occurs in precursor polymers and the release of small molecule by-products. One advantage of these large endothermic enthalpies (ΔH) is that the reaction acts as a heat sink to slow down combustion (Kubota and Nakanishi, 1964).

Thermogravimetric analysis of precursor polyblends revealed significant weight losses due to cyclization (T_1) at 255-400 °C (11 %) for pure PHA and 145-250 °C (9 %) for pure PAA as shown in Fig. 4. The weight loss (T_1) of the precursor blends was 18-20 % and occurred between 140 and 300 °C (Table 3). As mentioned earlier, the first-stage weight reduction (T_1) is brought about by the releasing of water molecules during heterocyclization.

These observed weight losses apparently correspond to endothermic transitions in the DSC thermograms as shown in Fig. 1. Initial decomposition onset points (T_2) of the polyblends increased from 532 to 540 °C with increasing PHA content (Table 3).

Table 3. Thermogravimetric Analysis of the Polyblend Films

PHA/PAA wt%	T_1^a °C	Wt. Red. ^b %	T_2^c °C	wtR900 ^d %
100/0	255	11(10) ^e	577	45
75/25	145	20	540	44
50/50	144	18	537	45
25/75	146	18	532	45
0/100	145	9(9)	533	41

^a1st weight reduction onset temperature.

^bWeight reduction between 140 °C and 400 °C in TGA thermogram.

^c2nd weight reduction onset temperature.

^dWeight percent of residue at 900 °C.

^eValues in parentheses represent calculated value.

Thermogravimetric analysis results for precursor polyblends (50/50 PHA/PAA) annealed at different temperatures are listed in Table 4. The TGA data indicates that the thermal stability increased steadily with increasing annealing temperature. However, it is noteworthy that T_1

increased from 144 to 272 °C with increasing annealing temperature from 25 to 250 °C. Also the weight residue at 900 °C increased from 45 to 57 % as annealing temperature increased (Fig. 5). Here the good thermal stability of precursor blends, as previously shown in Table 3 and Fig. 4, is also evident.

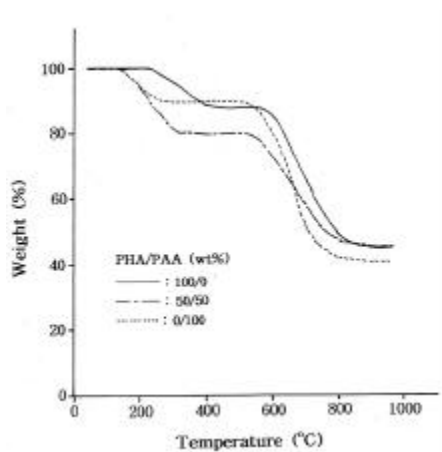


Figure 4. TGA thermograms of PHA, PAA, and 50/50 polyblends.

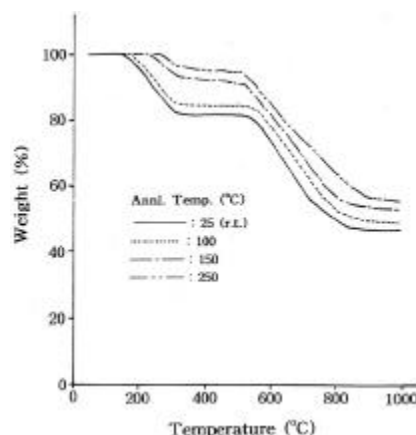


Figure 5. TGA thermograms of PHA/PAA (50/50) at different annealed temperature for 30 min.

Table 4. Thermogravimetric Analysis of the 50/50 PHA/PAA Films Annealed for 30 Minutes at Different Temperatures

Annl. Temp. °C	T ₁ ^a °C	Wt. Red. ^b %	T ₂ ^c °C	wtR900 ^d %
25 (r.t.)	144	18	537	45
100	172	15	540	49
150	223	6	542	54
250	272	3	531	57

^a1st weight reduction onset temperature.

^bWeight reduction between 140 °C and 400 °C in TGA thermogram.

^c2nd weight reduction onset temperature.

^dWeight percent of residue at 900 °C

Tensile properties

Tensile properties of the pure precursors and their blends are shown in Table 5, Figs. 6 and 7. The tensile strengths of the pure PHA and PAA at room temperature were found to be 137 and 84 MPa, respectively. There was no improvement in tensile strength on adding 25 % PHA to

a blend, while the strengths of the 50/50 and 75/25 PHA/PAA were 89 and 136 MPa, respectively.

Table 5. Tensile Properties of Polyblended Films Annealed for 3 Hours at Several Different Temperatures

Annl. Temp. °C	PHA/PAA wt%	Ult. Str. MPa	Ini. Modu. GPa	E. B.a %
25 (r.t.)	100/0	137	5.94	9
	75/25	136	5.34	27
	50/50	89	2.94	42
	25/75	84	2.93	58
	0/100	84	2.96	72
150	100/0	137	5.98	4
	75/25	145	3.81	5
	50/50	100	3.08	4
	25/75	94	3.04	5
	0/100	95	2.98	63
250	100/0	143	6.27	4
	75/25	169	3.18	4
	50/50	169	2.98	4
	25/75	169	3.05	4
	0/100	185	3.01	61

^aPercent elongation at break.

At low weight percentages of PHA in the polyblends, the blends exhibited tensile strengths close to that of the pure PAA, as PAA was the dominant phase or matrix. When the PHA loading was increased to 75 %, there was an obvious increase in the tensile strength, because PHA was now the dominant phase and PHA has a higher tensile strength than PAA.

Ultimate strength of polyblends annealed at 150 °C showed similar tensile behavior compared with samples at room temperature. The higher percent of PHA gave higher tensile strengths of the blends. In particular, the strength of the 75/25 PHA/PAA was higher than that of the pure PHA (145 MPa).

For the samples annealed at 250 °C, the strength of the pure PAA and their blends significantly improved compared with pure PHA. The strengths of pure PAA and pure PHA were 185 MPa and 143 MPa, respectively, and 169 MPa for the three polyblends. As described above, the PAA in the blend has fully cyclized to polyimide at 250 °C, whereas PHA has not been affected significantly at the same annealing temperature.

Similar to the trend in strength, the initial modulus of the blends stayed constant up to 50% PHA content for samples annealed at room temperature (2.93-2.96 GPa). Above 50 wt% in PHA the blend showed a tremendous improvement in the initial modulus as shown in Table 5 and Fig. 7. This is probably due to the rigid-rod aromatic character of the PHA in the polyblends. It is evident that the higher content of rigid-rod PHA plays an important role in this PHA/PAA system.

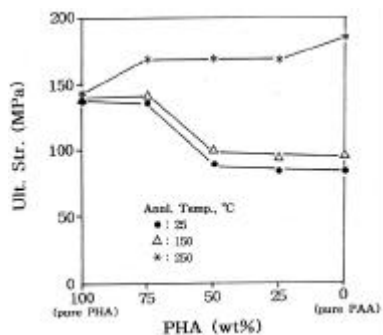


Figure 6. Ultimate strength of blends vs. PHA content at different annealed temperature.

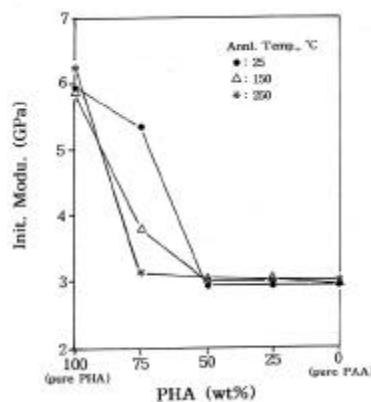


Figure 7. Initial modulus of blends vs. PHA content at different annealed temperature.

At constant annealing times (3hrs), as shown in Table 5, the initial modulus of pure PHA and pure PAA increased linearly from 5.94 to 6.27 GPa and from 2.96 to 3.01 GPa, respectively, with increasing annealing temperature from 25 to 250 °C. The effect of heat treatment on the initial modulus is shown in Fig. 7. For the samples annealed at 250 °C, initial modulus of the polyblends is nearly the same as that of PAA up to an initial 50 wt% PHA, further addition shows a dramatic increase in modulus to 100 wt% PHA.

Addition of PHA showed a decrease from 72 to 9% in elongation at break for room temperature annealed samples, as presented in Table 5. When the annealing temperature increased from 25 to 250 °C, the elongation at break of pure PAA decreased from 72 to 61%. On the other hand, there was no change in the elongation at break for polyblends with various PHA contents, when annealed at 150 °C and 250 °C. It was found to be near 4%. Upon heat treatment, the blends showed higher strength and moduli.

Overall, the tensile properties of precursor polyblends were significantly improved by the addition of PHA.

Morphology

The morphology of fractured specimens was examined to investigate the relationship between the mechanical properties and the resulting microstructure of PAA based composites. SEM micrographs of fracture surfaces of pure precursors and their precursor blends are shown in Fig. 8 and 9. Fig. 8a and 8e show the morphologies of the pure PHA and PAA, respectively. The PHA phase in all blends is typically 50 to 90 nm in diameter and appears to be uniformly distributed over the fracture surface (Fig. 8b-8d). The 25/75 PHA/PAA blend shows fine PHA particles 50-70 nm in diameter (Fig. 8d) and the 50/50 PHA/PAA blend also shows a fine dispersion with a domain size of 70-90 nm in diameter. More agglomerated PHA particles due to increasing PHA content are shown in Fig. 8c. When the PHA content increased to 75 wt%, however, the spherical domains of PHA turned to fibrillar domains, which was similar to pure PHA, with an average diameter of 40-50 nm as shown in Fig 8b. This is in agreement with the

mechanical property trends, in which the tensile strength and modulus drastically improved when the PHA content was 75 wt% (see Table 5). As shown in Fig. 8, the presence of any open space around the PHA domains was not observed in the SEM micrographs. However, occurrence of no open space for the blends does not imply good interfacial adhesion between PHA and PAA. Compatibility and transamidation of this system at various annealing temperatures will be reported later (Chang and Farris, unpublished).

Also, SEM micrographs of the 50/50 PHA/PAA polyblends with heat treatment at different annealing temperatures are shown in Fig. 9a-9f. For the blend annealed at 100 °C for 30 minutes (Fig. 9b), no changes were observed when compared with the unannealed sample.

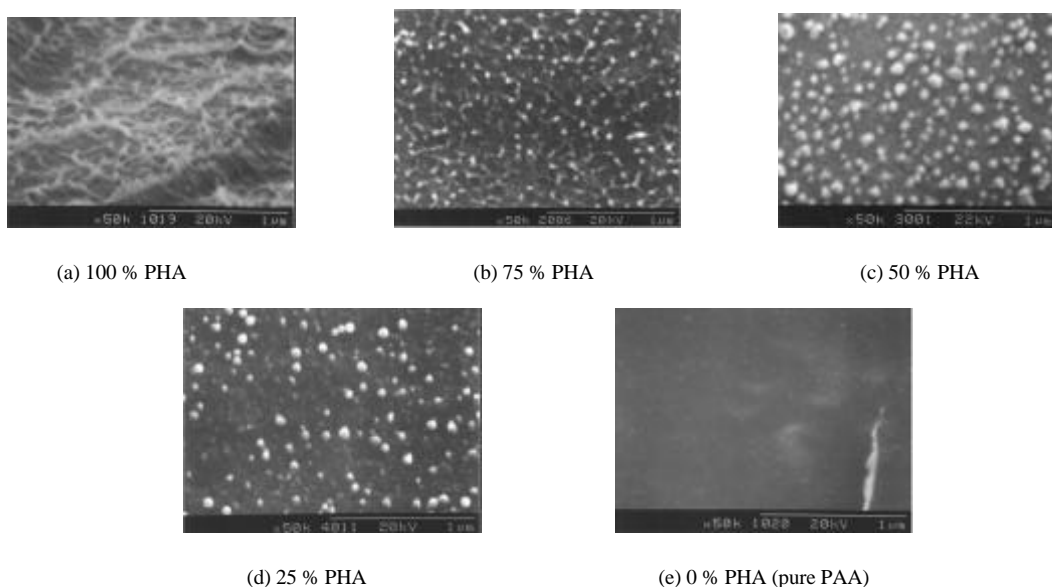


Figure 8. SEM micrographs of fracture surfaces of the films (x 50,000).

When annealed at 250 °C, finely dispersed fibrils of the PHA phase were present having diameters of 40-50 nm (Fig. 9c and 9d). Increasing the annealing temperature to 350 °C, the 50/50 blend showed a dimple-like structure probably due to partial cyclization of the PHA (Fig 9e). Fig. 9f shows a 50/50 PHA/PAA sample annealed at 450 °C, which is the cyclization temperature of PHA to form the fully heterocyclic polymer, PBO.

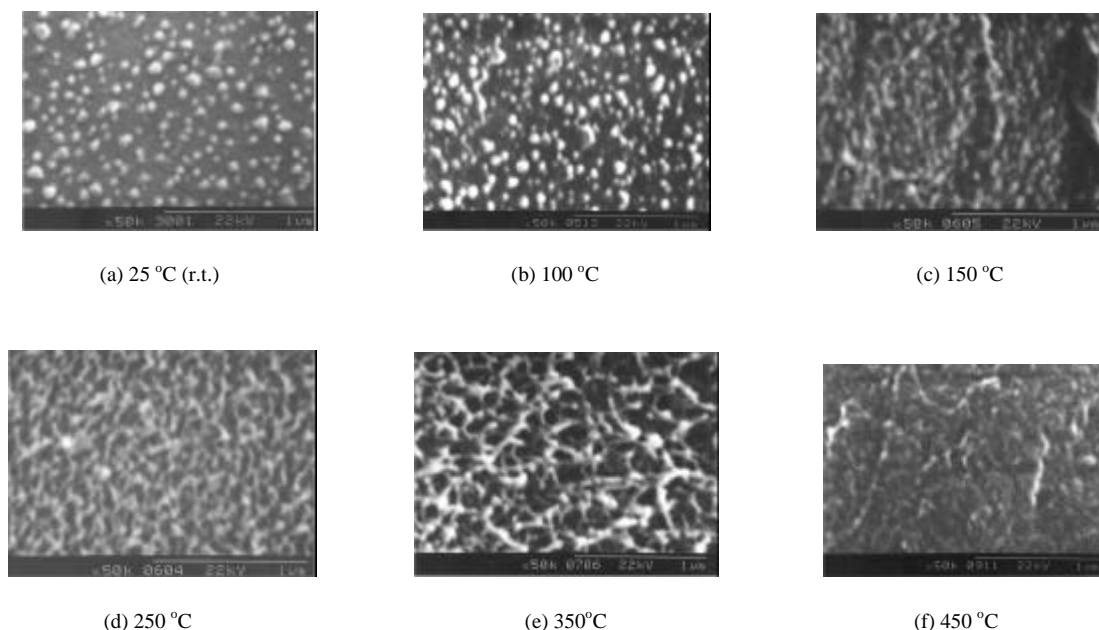


Figure 9. SEM micrographs of 50 % PHA films annealed at different temperature for 30 min (x 50,000).

Degree of Crystallinity

A rough estimate of the degree of crystallinity of the films was made from the areas of the crystalline and amorphous diffractions (Rabek, 1980). Typical X-ray diffractograms of the composites are shown in Fig. 10. Diffraction from the 25/75 PHA/PAA is similar to that of the pure PAA. However, when the PHA content was increased to 75%, the diffraction peaks due to pure PAA at $2\theta = 10^\circ$ and 15° disappeared. While, a medium new diffraction was observed at $2\theta = 17^\circ$ in pure PHA. A sharp and strong diffraction at $2\theta = 8^\circ$ did not change regardless of the PHA content in all the polyblends.

Fig. 11 shows the X-ray diffractograms of 50/50 PHA/PAA at different annealing temperatures. Diffractions from blends when annealed from 100 to 250 °C are similar to that of the unannealed blend. It is assumed that the heterocyclization of PAA precursor did not contribute to the crystallinity changes of the composites. For annealing temperatures up to 450 °C, two new diffractions were observed at $2\theta = 13^\circ$ and 17° due to the complete cyclization of PHA.

Degree of crystallinity of the films increased from 10 to 30% with increasing PHA content for unannealed samples. For the 50/50 PHA/PAA, the crystallinity increased linearly from 28 to 50% with increasing annealing temperature from 100 to 450 °C (Table 6).

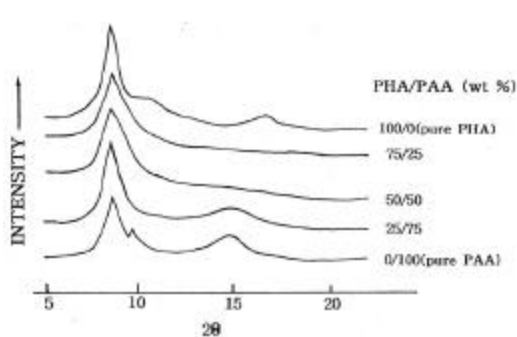


Figure 10. X-ray diffractograms of polyblends.

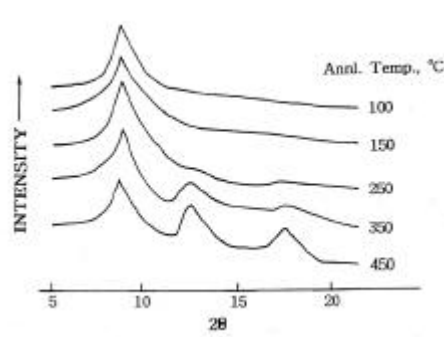


Figure 11. X-ray diffractograms of PHA/ PAA (50/50) annealed at different temperatures.

Table 6. Degree of Crystallinity of Pure Precursors and Their Polyblends at Different Annealing Temperatures

Annl. Temp., °C	PHA/PAA, wt%	D. C., ^a %
25 (r.t.)	100/0	30
	75/25	23
	50/50	19
	25/75	12
	0/100	10
100	50/50	28
150		33
250		37
350		43
450		50

^aDegree of crystallinity.

From the relationship between degree of crystallinity and annealing temperature, it can be seen that the degree of crystallinity increased with the annealing temperature due to the heterocyclization of the precursors. This result shows the correlation between the morphology of the blends and measured tensile properties (Table 5).

Biaxial stress using holographic interferometry

The radius of the membrane is 2.050 cm and the film density is 1.368 g/cm³ for PHA, 1.375 g/cm³ for PAA, and 1.370 g/cm³ for 50/50 PHA/PAA. The number of the zero and the order of the Bessel function is determined directly from the observed vibration pattern at a given frequency. The indices *m* and *n* represent the number of radial and tangential nodal lines, respectively. The relationship between frequency and stress is independent of film thickness and all material parameters except density.

Table 7. Residual Biaxial Stress for the Precursor Membranes Tested in a Vacuum

No	m, n	Z_{mn}	PHA		PHA/PAA (50/50)		PAA	
			Freq. sec ⁻¹	Stress MPa	Freq. sec ⁻¹	Stress MPa	Freq. sec ⁻¹	Stress MPa
1	0, 1	2.405	1385	7.31	1683	11.13	2650	27.70
2	1, 1	3.831	2102	6.85	2719	11.44	4185	27.22
3	2, 1	5.138	2846	6.97	3746	12.08	5635	27.44
4	3, 1	6.380	3612	7.28	4592	11.77	7013	27.56
5	4, 1	7.586	4390	7.61	5510	11.99	8315	27.41
6	2, 2	8.417					9170	27.01

As seen in Table 7, the biaxial stresses of the PHA, PAA, and 50/50 PHA/PAA are 6.85-7.61 MPa, 27.01-27.70 MPa, and 11.13-12.08 MPa, respectively, with increasing frequencies. In particular, the biaxial stress of the 50/50 PHA/PAA was lower than the expected value. This may be attributed to poor miscibility of the two precursor polymers in blending (Dutta et al., 1990). A few examples of typical holographic patterns are shown in reference (Chang et al., 1998). For the same membrane sample, higher resonant modes can be excited at specific resonant frequencies, but all of them show a constant stress value. A plot of biaxial stresses for the PHA, PAA, and the blended membrane is shown in Fig. 12.

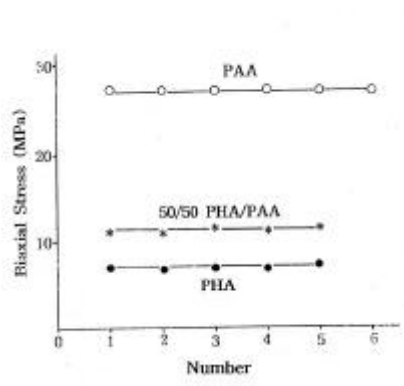


Figure 12. Calculated biaxial stresses for PHA, PAA, and PHA/PAA (50/50) membranes.

CONCLUSIONS

This study attempts to illuminate the thermal and mechanical properties of precursor composites from a PBO precursor, PHA, and a PI precursor, PAA, through solution blending. Moreover, the different thermal histories used to obtain the results produce different morphologies and consequently different mechanical behavior in the composite materials.

Precursor polyblends showed large thermal endothermic peaks. These large endothermic cyclizations play an important role in flame retardancy by acting as a heat sink as well as releasing flame quenching molecules such as water upon heating. Those heterocyclic endotherms decreased with increasing annealing temperature. Annealing enhanced the thermal properties, degree of crystallinity, and the mechanical properties of the precursor polyblends. From SEM micrographs of the blended films, a highly dispersed PHA phase was observed in a matrix PAA phase with domain size of 40-90 nm in diameter and the blended films were optically transparent for all compositions.

Holographic interferometry is a valuable technique for resolving the state of stress in membranes. Special sample preparation techniques have been designed to preserve the state of stress in the membrane. Measured and predicted mode shapes are in very close agreement.

ACKNOWLEDGMENTS

This study was supported by the Federal Aviation Administration (FAA).

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